

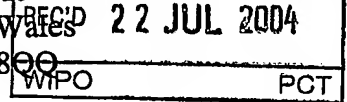


6304/2349



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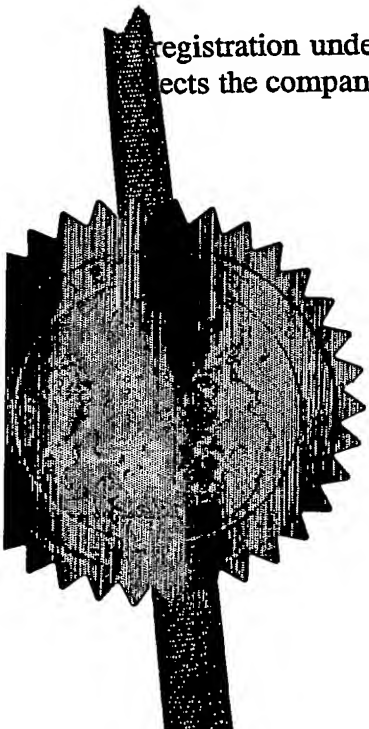
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Andrew Gorse

Dated

8 July 2004





1/77

04 JUN 2003

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P01/7700 0.00-0312781.8

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference P33300-/MGO/CWA

2. Patent application number
(The Patent Office will fill in this part) 04 JUN 2003 0312781.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)
Ythan Environmental Services Limited
Unit 1, Castle Street
Castlepark Industrial Estate
Ellon
AB41 9RF

086 450 20001

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention "Method"

5. Name of your agent (if you have one) Murgitroyd & Company
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)
Scotland House
165-169 Scotland Street
Glasgow
G5 8PL

Patents ADP number (if you know it) 1198015

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

1 **METHOD**

2

3 This invention relates to a method of insulating
4 submerged conduits, particularly but not exclusively
5 those adapted to transfer fluids from subsea
6 hydrocarbon reservoirs to a service platform.

7

8 A plurality of conduits or pipes of relatively small
9 diameter typically extend from a seabed structure to
10 a service platform and are enclosed within an outer
11 'carrier' pipe. Such an arrangement is known as a
12 'pipeline bundle', and is adapted to convey produced
13 fluids from the well.

14

15 When fluids are extracted from subsea reservoirs,
16 their temperature is normally higher than that of
17 the surrounding water. As the fluids cool in the
18 pipes to the temperature of the water, certain
19 compounds come out of solution, and this causes
20 problems with precipitates such as waxes or gas
21 hydrates that build up within the pipelines and can

1 reduce or prevent the flow of hydrocarbons.

2 Moreover, the viscosity of the produced fluids
3 increases as their temperature decreases, which also
4 reduces the rate of flow through the pipeline.

5

6 It is known to insulate pipeline bundles in several
7 ways to offset these problems - for instance pipes
8 are often insulated using solid synthetic foam
9 preformed insulating coatings. Alternatively the
10 pipe-in-pipe annular spaces are evacuated, or are
11 filled with silica-based materials or hollow spheres
12 of plastic material in a synthetic resin matrix.

13

14 These and similar techniques have serious
15 disadvantages in the way of investment cost,
16 difficulty of handling, and the requirement for
17 specialist equipment to manufacture the materials,
18 and as a consequence the materials needed for the
19 techniques are not routinely made up at the point of
20 manufacture of the pipeline. Also some of the
21 materials needed for the insulation are limited with
22 respect to the depth of water in which they can be
23 applied. For example, at depths beyond around 1500
24 metres the hydrostatic pressure of the water column
25 will collapse foam and its insulating qualities will
26 be lost.

27

28 A further attempt to solve this problem is disclosed
29 in European Patent Publication N° 0,336,493. In
30 this application, a liquid hydrocarbon gel is
31 provided in the outer pipe to insulate the smaller
32 diameter pipes running therethrough. However, the

1. use of a fluid gel requires the provision of a
2 pressure balancing system which is prone to failure.

3

4 According to the present invention, there is provided
5 a method of insulating a conduit, the method
6 comprising:

7

8 injecting a substance into a first conduit, the
9 first conduit enclosing at least one second
10 conduit;

11

12 allowing said substance to form a gel which has
13 a dynamic viscosity of more than 2000Pa.S.

14

15 Preferably, the conduits are tubulars, such as
16 oilfield tubulars.

17

18 Preferably, the substance is injected into an
19 annular space between the first and second conduits.

20

21 Preferably, the gel can retain its integrity
22 unsupported.

23

24 In this context, 'retain its integrity unsupported'
25 means a gel that can, for example, be sliced into
26 pieces and can maintain its form when dropped from a
27 height, but cannot be poured or pumped.

28

29 Preferably, the substance is a pourable fluid prior
30 to gellation.

31

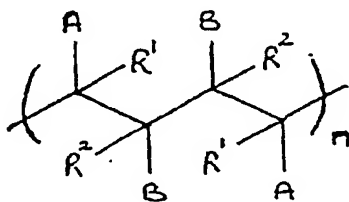
Dynamic viscosities of gelled materials discussed in this patent are considerably in excess of 1000 Pa.S, preferably 2000 Pa.S - 100,000 Pa.S.

Preferably, the substance comprises a fluid which has a comparatively high specific heat capacity and a second fluid which has a comparatively low thermal conductivity.

More preferably, the first fluid is water and the second fluid is a hydrophobic fluid such as a hydrocarbon-containing fluid or a vegetable oil.

The relative proportions of the first and second fluids can be adjusted depending on the nature of the hydrocarbons being recovered, the specific pipeline arrangement and the subsea environment.

Preferably, the substance further comprises a first and second polymeric compound. The first polymeric material may have a general formula

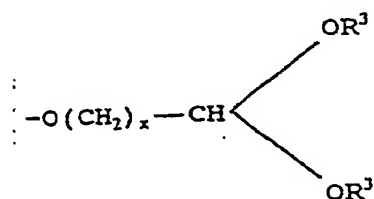


wherein A and B are the same or different wherein at least one comprises a relatively polar atom or group and R^1 and R^2 independently comprise relatively non-polar atoms or groups.

1 Preferably, R^1 and R^2 are hydrogen atoms although
 2 they may be other relatively non-polar atoms or
 3 groups, for example, alkyl groups.

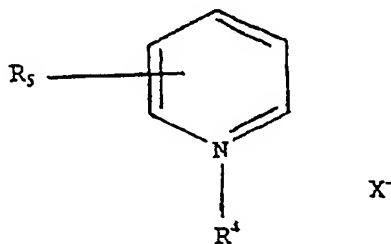
4
 5 Preferably, A and B are independantly selected from
 6 optionally-substituted alkyl, cycloalkyl,
 7 cycloalkenyl, cycloalkynyl, aromatic and
 8 heteroaromatic groups.

9
 10 More preferably, A represents a phenyl group
 11 substituted, preferably at the 4-position relative
 12 to the group C-C, by a formyl group or a group of
 13 general formula:



14
 15
 16
 17
 18
 19 wherein x is an integer from 1 to 6 and each R^3 is
 20 independently an alkyl or phenyl group or together
 21 form an alkalene group.

22
 23 More preferably, group B represents a group of
 24 general formula:



1 wherein R⁴ represents a hydrogen atom or an alkyl or
2 aralkyl group, R⁵ represents a hydrogen atom or an
3 alkyl group and X⁻ represents a strongly acidic ion.

4
5 Other options for the groups A, B and R¹ - R⁵ are
6 disclosed in British Patent Publication GB
7 2,317,895A the disclosure of which is incorporated
8 herein by reference.

9
10 Preferably, the second polymeric substance includes
11 one or more functional groups capable of reacting
12 with said first polymeric compound.

13
14 More preferably, the second polymeric compound
15 includes a functional group selected from an
16 alcohol, carboxylic acid, carboxylic acid
17 derivative, for example an ester, and an amine
18 group.

19
20 Even more preferably, the second polymeric substance
21 is selected from optionally substituted
22 polyvinylalcohol, polyvinylacetate, polyalkalene
23 glycols and collagen (and any component thereof).

24
25 Yet more preferably the second polymeric material is
26 polyvinyl alcohol. Other possible second polymeric
27 materials are disclosed in the aforementioned
28 British Patent Publication 2,317,895A.

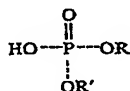
29
30 The substance may further comprise acid, such as
31 paratoluene sulphuric acid, to catalyse the reaction

1 between the first and the second polymeric
2 compounds.

3
4 In alternative embodiments, the substance may
5 comprise a third polymeric material and a ferric
6 salt in addition to a hydrocarbon. Such alternative
7 embodiments preferably do not comprise the first and
8 second polymeric compounds nor water. Preferably
9 therefore, the alternative embodiments are effected
10 in a hydrocarbon phase.

11
12 Preferably, the third polymeric material is a
13 phosphate, more preferably an orthophosphate, even
14 more preferably an orthophosphate ester.

15 Preferably, the orthophosphate esters have the
16 structure of formula:



17
18
19
20 wherein R is a straight or branched chain alkyl or
21 alkaryl group having about 6 to about 18 carbon
22 atoms and R' is hydrogen or an aryl, alkaryl or
23 alkyl group having about up to 18 carbon atoms.

24
25 Preferably, about 0.3% to 1.5 wt% by weight, based
26 on the hydrocarbon/water liquid, of the phosphate is
27 added.

28
29 Preferably, the ferric salt and third polymeric
30 material are added in an equimolar ratio. More
31 preferably, the alternate embodiment forms a gel as

1 described in US Patent 5,417,287, the disclosure of
2 which is incorporated herein by reference.

3

4 Preferably, materials which undergo a change in
5 phase (such as going from liquid to solid) on
6 cooling are selected, as these release heat thereby
7 extending the time it takes for the tubular contents
8 to cool down.

9

10 Optionally, cenospheres may be added to the
11 substance in order to reduce thermal conductivity
12 and improve mechanical strength.

13

14 Optionally, antibacterial agents and/or corrosion
15 inhibitors can be added to the substance.

16

17 According to a second aspect of the present
18 invention, there is provided a method of insulating
19 a submerged conduit, the method comprising the steps
20 of:

21 applying at least one substance to the conduit
22 before it is submerged; then,
23 submerging the conduit under water; and
24 allowing the substance to form a gel.

25

26 Preferably the method employs the methods set out
27 above.

28

29 Preferably, the tubular comprises further tubulars
30 enclosed therein.

31

1 Preferably, the substance is applied to an annulus
2 between the tubular and the said further tubulars
3 enclosed therein.

4
5 Embodiments of the present invention will now be
6 described by way of example only.

7
8 Example 1

9
10 To test the effectiveness of such a gelled fluid
11 insulating system as an insulator for a pipeline
12 bundle the following experiment was carried out. 45g
13 of oil (for example sunflower or vegetable oil) were
14 placed in a container to which 35g of cenospheres
15 were added and the mixture was stirred for five
16 minutes until the cenospheres were fully dispersed.

17
18 Cenospheres are small glass hollow spheres of
19 between 20 - 150 microns such as can be extracted
20 from volcanic ash or the ash from coal-fired power
21 stations. The addition of cenospheres reduces
22 thermal conductivity and improves mechanical
23 strength of the resulting gel. However they are not
24 essential to the invention.

25
26 In a separate beaker a mixture of 18g of water and
27 2g of polyvinylalcohol (PVA) was made up and the
28 mixture of sunflower oil and cenospheres was poured
29 into this and mixed together to form an emulsion
30 mixture of oil, water, PVA and cenospheres.

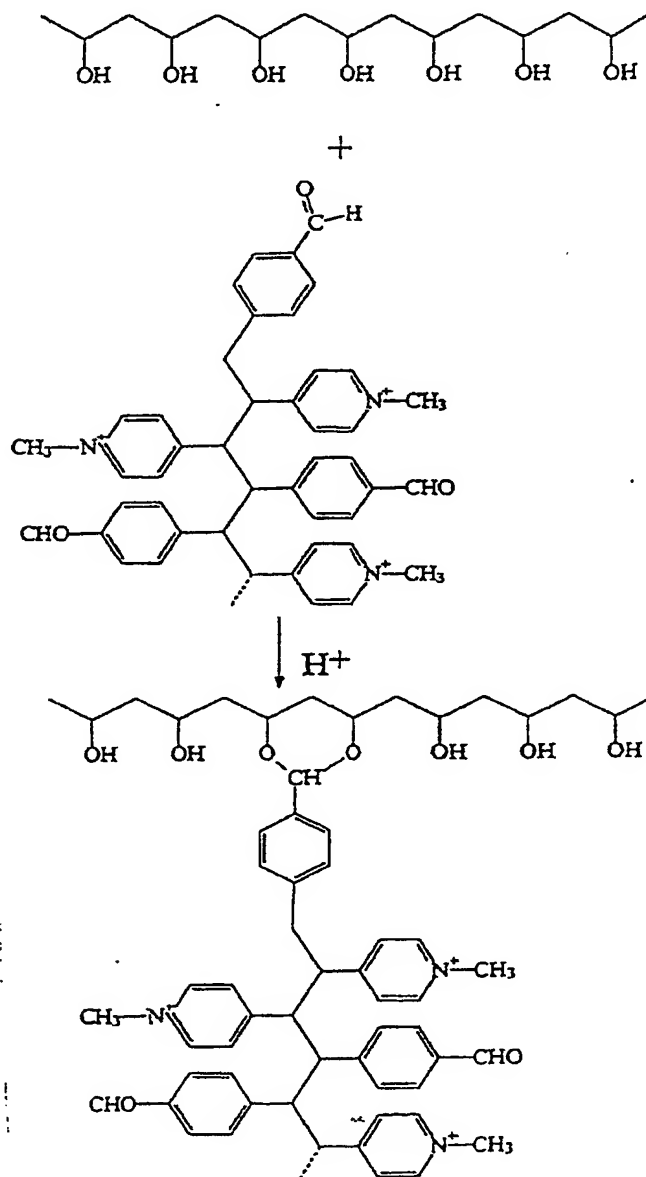
31

1 British Patent publication GB 2,317,895A discloses a
2 substance and a method of forming a gel, the
3 disclosure of which is incorporated herein by
4 reference.

5
6 An aqueous solution of 4-(4-formylphenylethenyl)-1-
7 methylpyridinium methosulphonate (SbQ) was added to
8 the mixture as a cross-linking agent. The resulting
9 mixture was then stirred and the contents of the
10 beaker were decanted into a 100ml measuring
11 cylinder. An acid was then added to catalyse the
12 change of phase of the mixture from liquid to gel.
13 An inorganic or organic acid may be used, examples
14 being hydrochloric acid, sulphuric acid, acetic
15 acid, and formic acid. The greater the quantity of
16 acid which is used, the quicker the rate of
17 formation of the gel. Thus the rate of formation of
18 the gel can be controlled by varying the amount of
19 acid used. The mixture was allowed to stand for a
20 period of twelve hours after which time a reaction
21 had occurred and a gel had formed.

22
23 An aldol condensation reaction between polymer
24 chains is effected to form the gel, that is a
25 reaction between the polyvinylalcohol and the SbQ
26 according to the reaction scheme below:

27
28
29
30
31
32



A determination of this material's thermal conductivity was carried out using a Huskaflux non-steady-state probe. The density was measured and the specific heat capacity was calculated from existing known values for each constituent in order to

1 determine the thermal diffusivity of the gelled
2 system.

3

4 Table 1 below details the thermal performance of
5 example 1.

6

7 Example 2

8

9 A second gelled fluid insulating system containing
10 76.5g of water, 8.5g of polyvinyl alcohol, 10g of
11 sunflower oil and 5g of cenospheres was similarly
12 made up, following the method of example 1.

13

14 0.5g of SbQ and 1g of acid (HCl 10%) was then added.

15

16 After a period of time, typically between one and
17 twenty four hours, the mixture sets as a solid
18 jelly-like material by undergoing the equivalent
19 aldol condensation reaction detailed above.

20

21 Some properties of this gel are set out in table 1,
22 below.

23

24 Example 3

25

26 A third all oil system using different chemistry was
27 made up according to a method described in US patent
28 5,417,287 the disclosure of which is incorporated
29 herein by reference.

30

31 16g of cenospheres were stirred into a container
32 holding 84g of kerosene. To this mixture 1g

1 Clearwater HGA 70 (an orthophosphate ester) was
2 added (although between 0.3 and 1.5% by weight is
3 suitable). The mixture was gelled by the addition of
4 1g of Clearwater HGA 65 (a ferric salt).
5 Alternatively ferric sulphate may be added at
6 between 0.25 to 2.0 moles per mole of phosphate
7 ester. The fluid was left to gel for a period of 24
8 hours. In practice however a gel formed typically
9 between 2-5 minutes from adding the ferric source.

10

11 Some of the properties of this gel are set out in
12 table 1 below which also shows a range of gelled
13 fluid insulating systems with different mixes of
14 oil, water and cenospheres.

15

16 Example 4

17

18 A fourth gelled fluid insulating system containing
19 10g of water, 1g of polyvinyl alcohol, 45g of
20 sunflower oil and 45g of cenospheres was similarly
21 made up, following the method of example 1.

22

23 0.05g of SbQ and 1g of acid (HCl 10%) was then
24 added.

25

26 After a period of time, typically between one and
27 twenty four hours, the mixture sets as a solid
28 jelly-like material by undergoing the equivalent
29 aldol condensation reaction detailed above.

30

31 Some properties of this gel are also set out in
32 table 1, below.

1
2 In general the relative proportions of components in
3 the gelled fluid insulating medium were determined
4 using considerations of cost, ease of shipping to
5 manufacturing location and desired performance
6 characteristics.

7
8 Of particular interest is a measure of the rate of
9 cool down known as diffusivity, this is described
10 as:

11
12
$$\text{Diffusivity} = \frac{\text{Conductivity (W/mK)}}{[\text{Specific heat capacity (J/kg/K)} \times \text{Density kg/m}^3]}$$

14
15 The diffusivity measurements are given in table 1
16 below.

17
18

Gel	Ratio of Components				Conductivity ^[3] W/mK	Specific Heat ^[2] J/kgK	Density ^[2] kg/m ³	Diffusivity m ² /s
	Oil ^[1]	Water	Other	Cenospheres				
1	45	18	2 PVA + 0.125 SbQ + 1 acid	35	0.22	1870	908	0.130 x 10 ⁻⁶
2	10	76.5	8.5 PVA + 0.5 SbQ + 1 acid	5	0.44	3790	982	0.118 x 10 ⁻⁶
3	84 ^[4]	0	1 C'HGA 70 (phosphate ester) 1 C'HGA 65 (ferric salt)	16	0.14	1740	863	0.093 x 10 ⁻⁶
4	45	10	1 PVA + 0.05 SbQ + 1 acid	45	0.17	1480	901	0.127 X 10 ⁻⁶

1 Table 12 Notes:

- 3 [1] Samples based on sunflower oil.
4 [2] Estimated from available data for constituents.
5 [3] Conductivity was measured using a non steady state probe
6 [4] Oil based gel using paraffinic oil.

7
8 Abbreviations

- 9
10 PVA - Polyvinylalcohol
11 SbQ - 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphonate
12 OPE - Orthophosphate ester
13 C'HGA 70 - Clearwater HGA 70 (phosphate ester)
14 C'HGA 65 - Clearwater HGA 65 (ferric salt)
15

16 The gelled fluid insulating media thermal
17 conductivities and diffusivities (a measure of the
18 rate of cool down) are comparable to those of
19 existing syntactic materials, which can go down to
20 $0.12W/mK$ and $0.12 \times 10^{-6} m^2/s$ respectively. While
21 low conductivity is required to provide the steady
22 state thermal performance on the flowing system, low
23 diffusivity is also desirable to maintain long cool-
24 down times.

25

26 In use, the pipeline bundles are made up on the
27 surface as is conventional in the art and an
28 oil/water/additive mixtures for example, those
29 detailed in examples 1-4 above, are then added to
30 the pipe-in-pipe annular space between the inner
31 pipes and the carrier pipe. The bundles are then
32 installed in the conventional manner.

33

34 The mixture has a sufficiently low viscosity to
35 enable it to be pumped into the pipe-in-pipe bundle
36 annular space where a reaction can take place which
37 results in the mixture forming into a gel as defined
38 in the Larousse Dictionary of Science and Technology

1 1995 page 470, that is a substance with properties
2 intermediate between the liquid and the solid
3 states.

4
5 The resulting gelled material is a jelly-like
6 substance and so can transmit the hydrostatic
7 pressure upon the external tubular or 'carrier' to
8 the inner tubulars. A further benefit of certain
9 embodiments of the present invention in using such
10 gelled fluid insulating media in pipe-in-pipe
11 systems is therefore that the external carrier pipe
12 does not need to be rated to hydrostatic pressure
13 experienced at depth since the gelled fluid
14 insulating media transfers the hydrostatic pressure
15 onto the inner tubulars.

16
17 A further consequence of certain embodiments of the
18 invention transmitting pressure is that they
19 maintain their integrity and insulating properties
20 unlike some prior art systems which can collapse and
21 lose their insulating properties at higher pressure.
22 Thus embodiments of the present invention do not
23 suffer the same depth limitations as syntactic foams
24 (although they will deform and recover at higher
25 stress).

26
27 The formation of a gel acts to prevent loss of heat
28 through convection. An advantage of certain
29 embodiments of the present invention is that the gel
30 possesses low conductivity, thereby providing
31 suitable insulating properties for deep water
32 applications.

1

2 A further advantage of certain embodiments of the
3 present invention is the high thermal mass and low
4 diffusivity of the gel which increases cool-down
5 times and gives operational flexibility for long tie-
6 backs and remote deep water production systems.

7

8 A further benefit of certain embodiments of the
9 present invention is that the thermal performance of
10 the gels, including conductivity and heat capacity,
11 can be varied and thus suitably tailored for
12 individual systems by varying the relative
13 components of oil, water and cenospheres. Thus
14 different compositions of the gels are used
15 depending on the specific nature of the fluids being
16 transported, the pipeline arrangement, the subsea
17 environment and other factors.

18

19 For instance, example 2 has a high specific heat
20 capacity making it suitable for applications where a
21 long cool down performance is required. Example 4
22 by contrast has a much lower thermal conductivity
23 and so it would be particularly suited to ensure
24 high pipeline fluid arrival temperatures thereby
25 easing fluid processing. Example 3 offers a balance
26 between thermal conductivity and good cool down
27 performance although it has a less favourable
28 environmental profile.

29

30 A further benefit of certain embodiments of the
31 present invention is the low toxicity and generally

1 non-hazardous materials which are used which
2 facilitates handling, transportation and disposal.

3
4 Moreover, the cost of certain embodiments of the
5 present invention is less than previous syntactic
6 'wet' coatings or silica based pipe-in-pipe systems,
7 they can be made on site and do not require
8 expensive storage or mixing facilities and a
9 pressure-rated outer carrier pipe is not required.

10
11 The thermal properties can be improved further by
12 selecting materials that undergo a change in phase
13 (such as going from a liquid to a solid) on cooling.
14 This change in phase will result in the release of
15 heat thereby extending the time it takes for the
16 pipeline contents to cool down.

17
18 Other chemicals such as anti bacterial agents, for
19 example DowTM Antimicrobial 7287, Avecia Proxel XL2
20 or Rhodia Tolcide PS50D, or corrosion inhibitors for
21 example imidazoline, amine salts or phosphate esters
22 can also be added to this gelled fluid insulating
23 medium.

24
25 Improvements and modifications may be made without
26 departing from the scope of the invention.